

# **An Inexpensive Reagent for Aldehyde to Alkyne Homologation**

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## **Supporting Information**

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## Experimental Section

**General.** All reagents were of commercial quality. MeCN was freshly distilled under nitrogen from sodium/benzophenone before use.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at 400 MHz.  $^{13}\text{C}$  multiplicities were determined with aid of a JVERT pulse sequence, differentiating the signals for methyl and methine carbons as “d”, for methylene and quaternary carbons as “u”. IR spectra were measured as neat oils.  $R_f$  values indicated refer to thin layer chromatography (TLC) on 2.5 x10 cm, 250  $\mu\text{m}$  analytical plates coated with silica gel GF. TLC solvent mixtures were volume/volume. MTBE is methyl *t*-butyl ether and PE is petroleum ether. All reactions were run under a nitrogen atmosphere and stirred magnetically.

### **1-(3-butyn-1-yl)-3-methoxy-benzene (2a)**

(Procedure B) Colorless oil, 76 mg, 0.47 mmol, 77% yield; TLC  $R_f$  = 0.67 (MTBE/PE, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (t, 1H,  $J$  = 7.7 Hz), 6.85 (d, 1H,  $J$  = 7.7 Hz), 6.79 (m, 2H), 3.82 (s, 3H), 2.85 (t, 2H,  $J$  = 7.6 Hz), 2.51 (td, 2H,  $J$  = 7.6, 2.6 Hz), 2.01 (t, 1H,  $J$  = 2.6 Hz);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  d 55.1, 111.6, 114.2, 120.8, 129.4; u 20.4, 34.9, 68.9, 83.8, 142.0, 159.6.

### **1-Ethynyl-2,3-dimethoxybenzene (2b)**

(Procedure A) Colorless oil, 128 mg, 0.79 mmol, 79% yield; TLC  $R_f$  = 0.49 (MTBE/PE, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (dd, 1H,  $J$  = 7.6, 1.6 Hz) \_ 7.00 (dd, 1H,  $J$  = 8.0, 7.6 Hz), 6.93 (dd, 1H,  $J$  = 8.0, 1.6 Hz), 3.95 (s, 3H), 3.87 (s, 3H), 3.27 (s, 1H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  d 55.9, 61.0, 113.4, 123.9, 125.5; u 79.7, 81.1, 116.8, 151.0, 152.6.

### **4-Methoxyphenylacetylene (2c)**

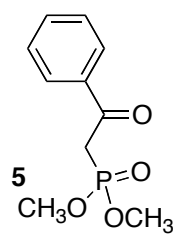
(Procedure B) Colorless oil (lit. mp = 25 °C), 82 mg, 0.62 mmol, 72% yield; TLC  $R_f$  = 0.62 (MTBE/PE, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.46 (m 2H), 6.84-6.87 (m, 2H), 3.82 (s, 3H), 3.01 (s, 1H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  d 55.3, 113.9, 133.6; u 75.8, 83.6, 114.1, 159.9.

### **2-Ethoxyphenylacetylene (2d)**

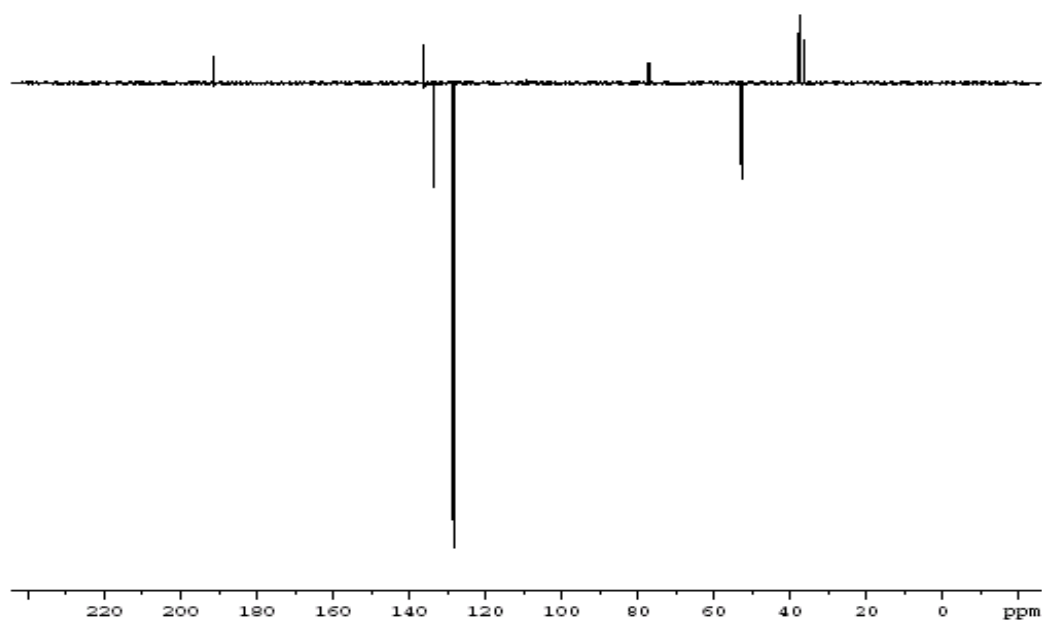
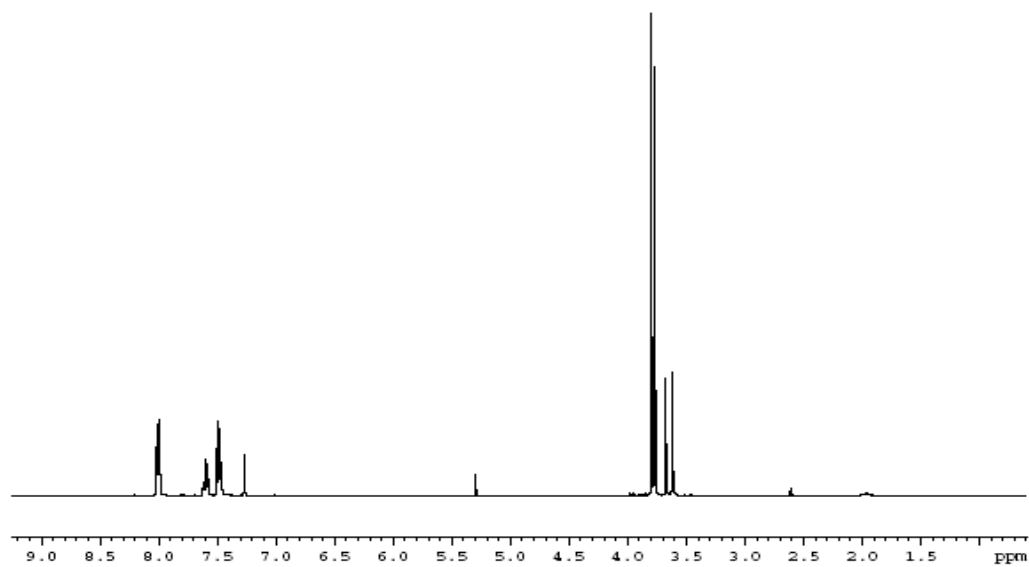
(Procedure B) Colorless oil, 94 mg, 0.64 mmol, 73% yield; TLC  $R_f$  = 0.69 (MTBE/PE, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (dd, 1H,  $J$  = 1.8, 7.5 Hz), 7.28-7.32 (ddd, 1H,  $J$  = 1.8, 7.5, 8.3 Hz), 6.90 (td, 1H,  $J$  = 7.5, 1.0 Hz), 6.88 (d, 1H,  $J$  = 8.3 Hz), 4.13 (q, 2H,  $J$  = 7.0 Hz), 3.30 (s, 1H), 1.48 (t, 3H,  $J$  = 7.0 Hz);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  d 14.6, 111.8, 120.2, 130.1, 134.1; u 64.2, 80.1, 81.0, 111.5, 160.0; IR 3284, 1595, 1490, 1251  $\text{cm}^{-1}$ ; MS 146 ( $\text{M}^+$ , 89), 131 (28), 118 (100); HRMS calcd for  $\text{C}_{10}\text{H}_{10}\text{O}$  146.0732, obsd 146.0731.

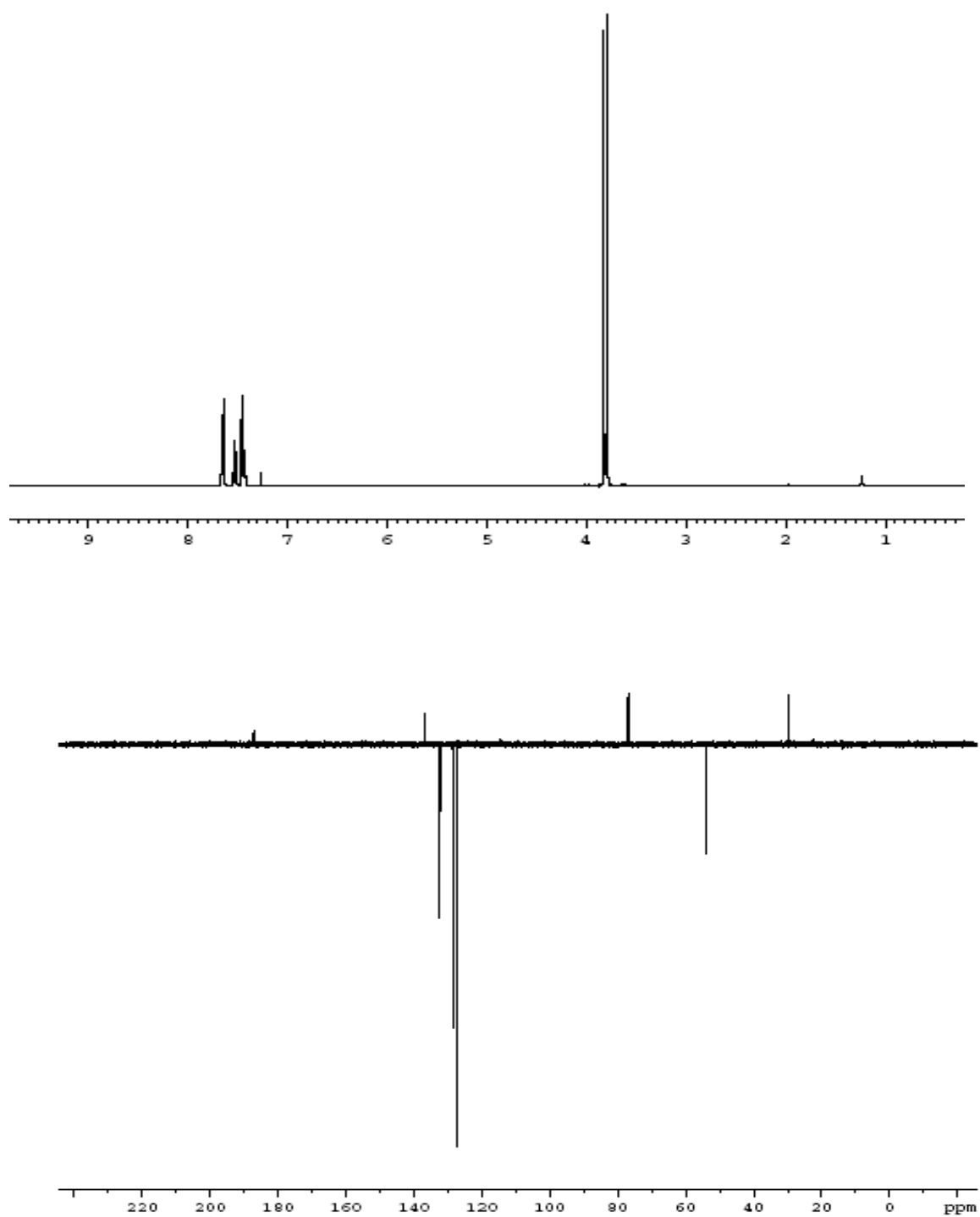
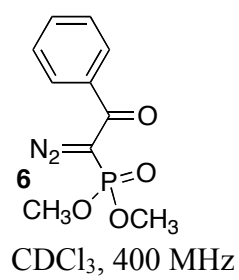
### **1-*O*-Benzyl-2,2-dimethyl-4-pentyn-1-ol (2e)**

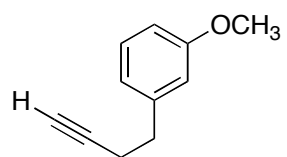
(Procedure B) Colorless oil, 77 mg, 0.41 mmol, 81% yield; TLC  $R_f$  = 0.73 (MTBE/PE, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.37 (m, 5H), 4.63 (s, 2H), 3.34 (s, 2H), 2.14 (s, 1H), 1.27 (s, 6H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  d 26.0, 127.4, 127.5, 128.4; u 32.2, 68.2, 73.3, 78.1, 90.2, 138.4; IR (film): 3298, 2979, 2861, 2062  $\text{cm}^{-1}$ ; MS: 187 ( $\text{M}^+ - 1$ , 7), 173 (18), 143 (100), 133 (57); HRMS calcd for  $\text{C}_{13}\text{H}_{16}\text{O}$  187.1123, obsd 187.1126.



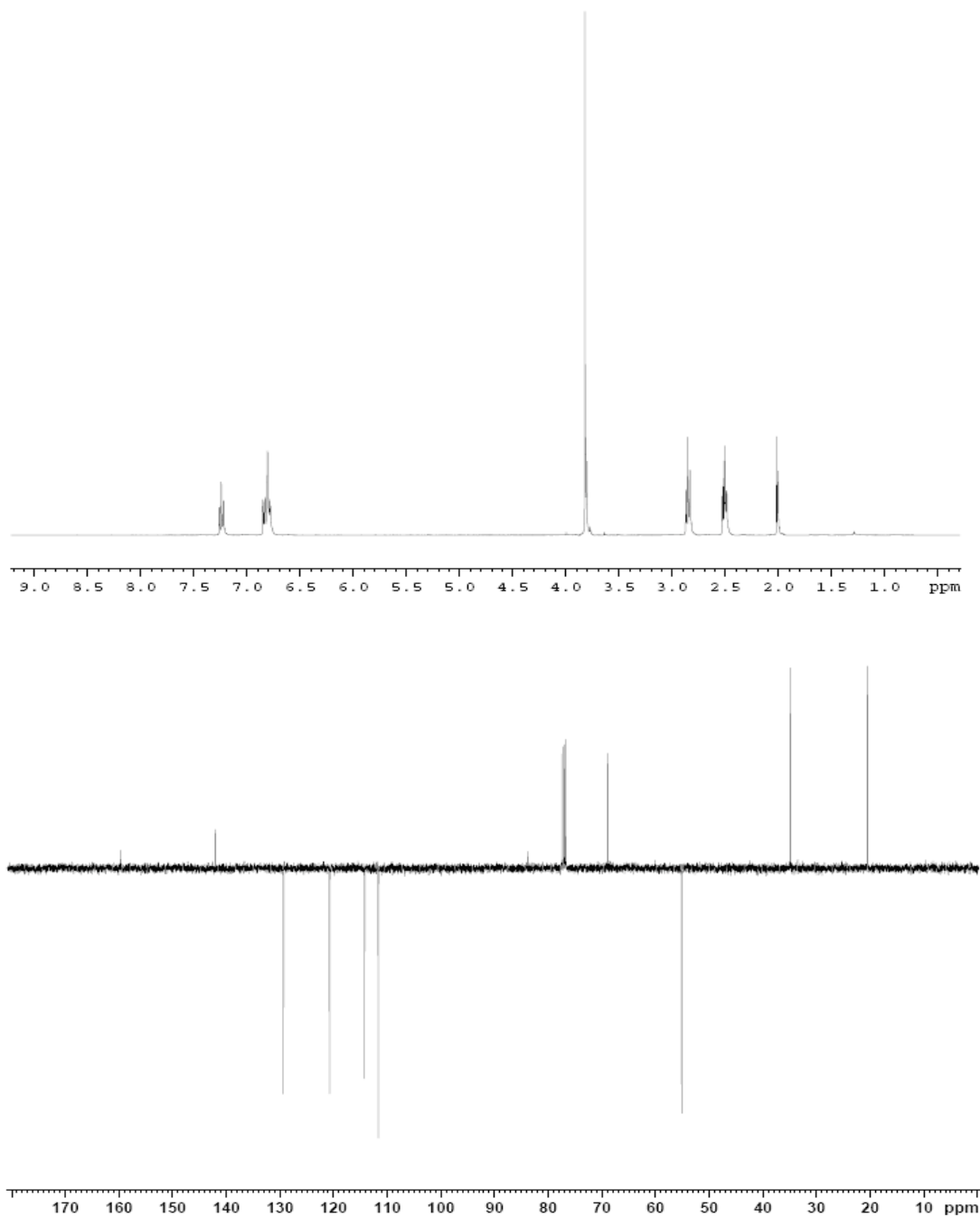
CDCl<sub>3</sub>, 400 MHz

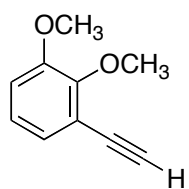




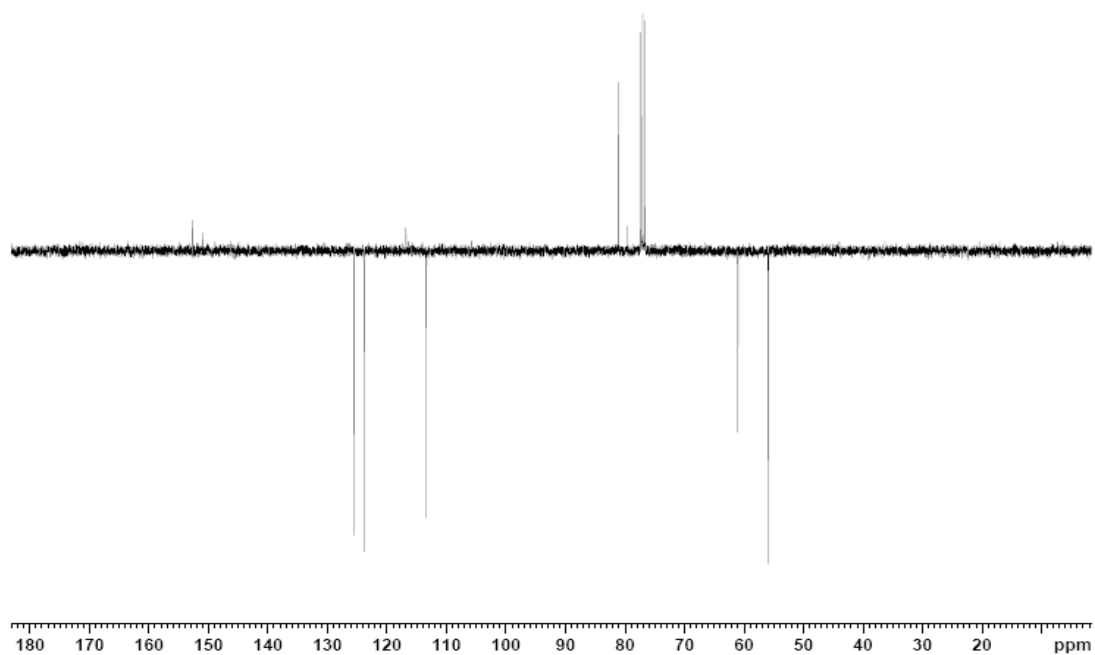
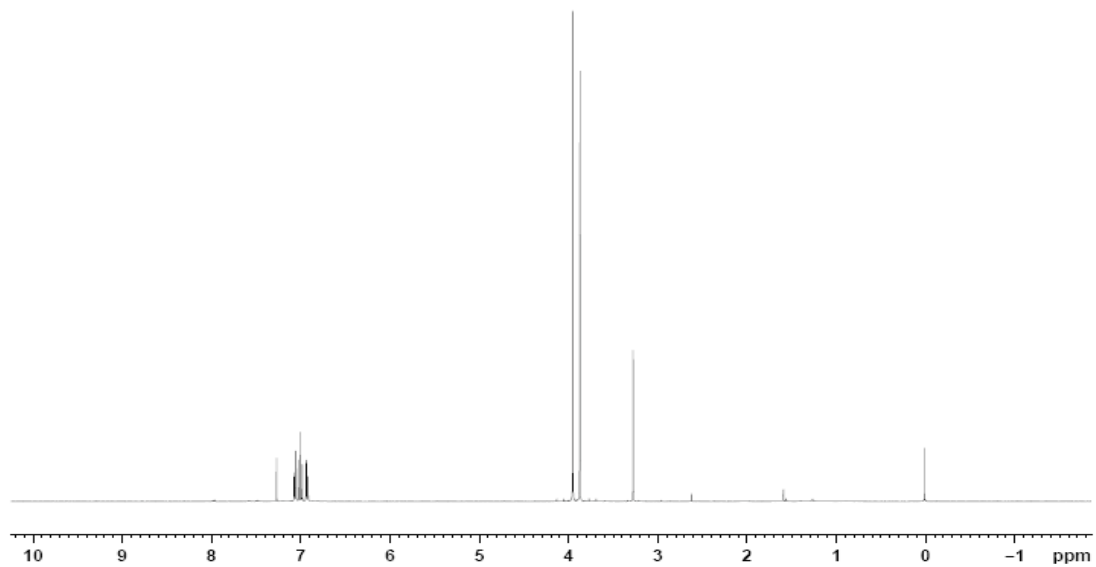


**2a** CDCl<sub>3</sub>, 400 MHz

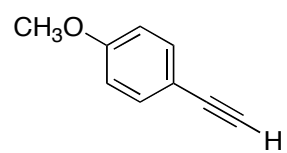




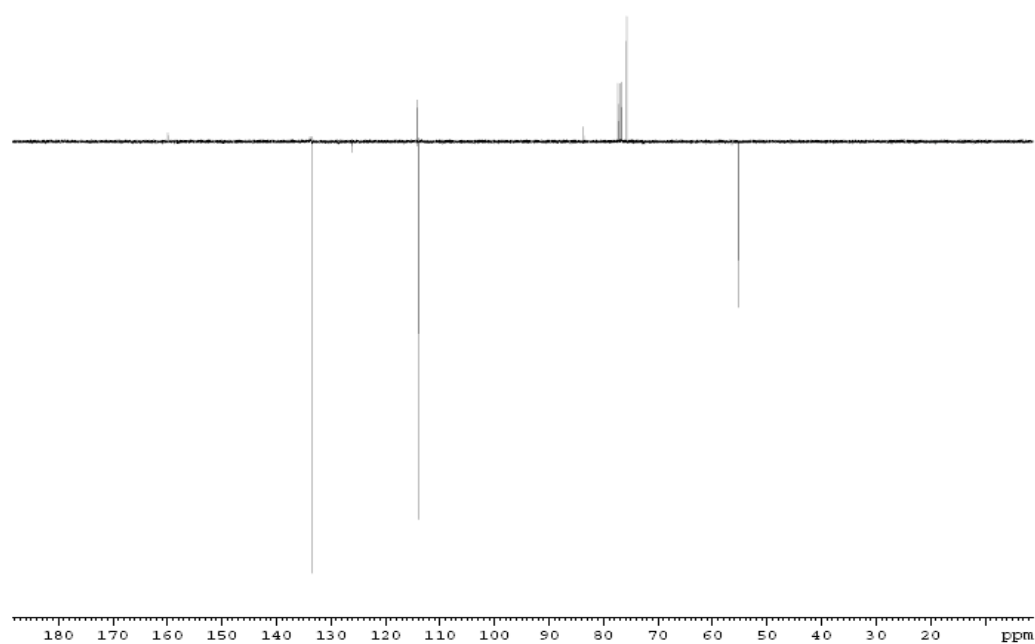
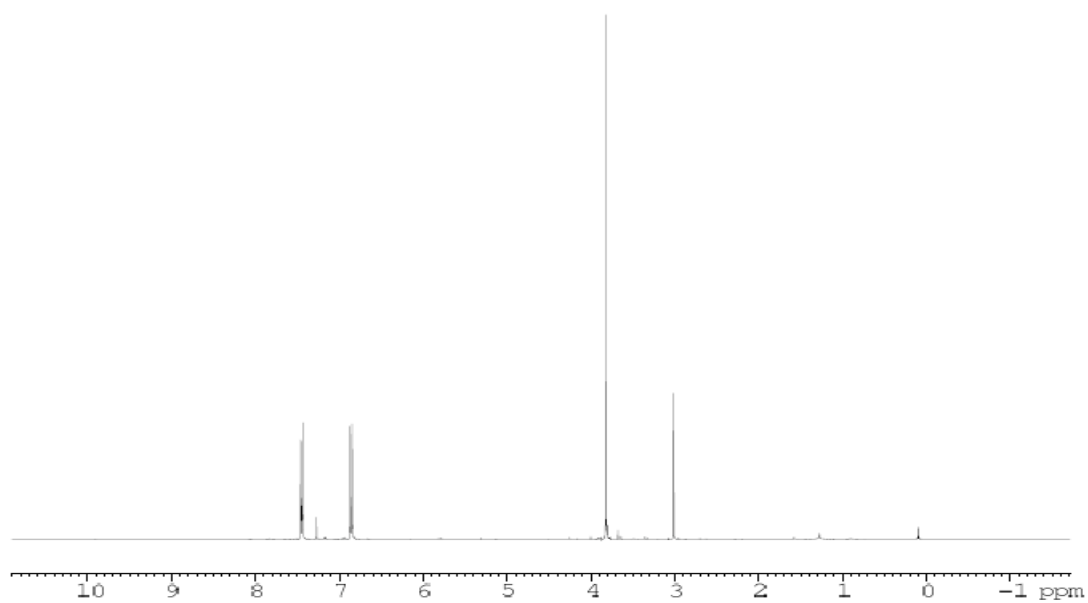
**2b** CDCl<sub>3</sub>, 400 MHz

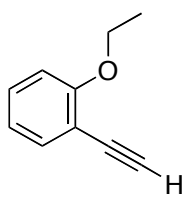




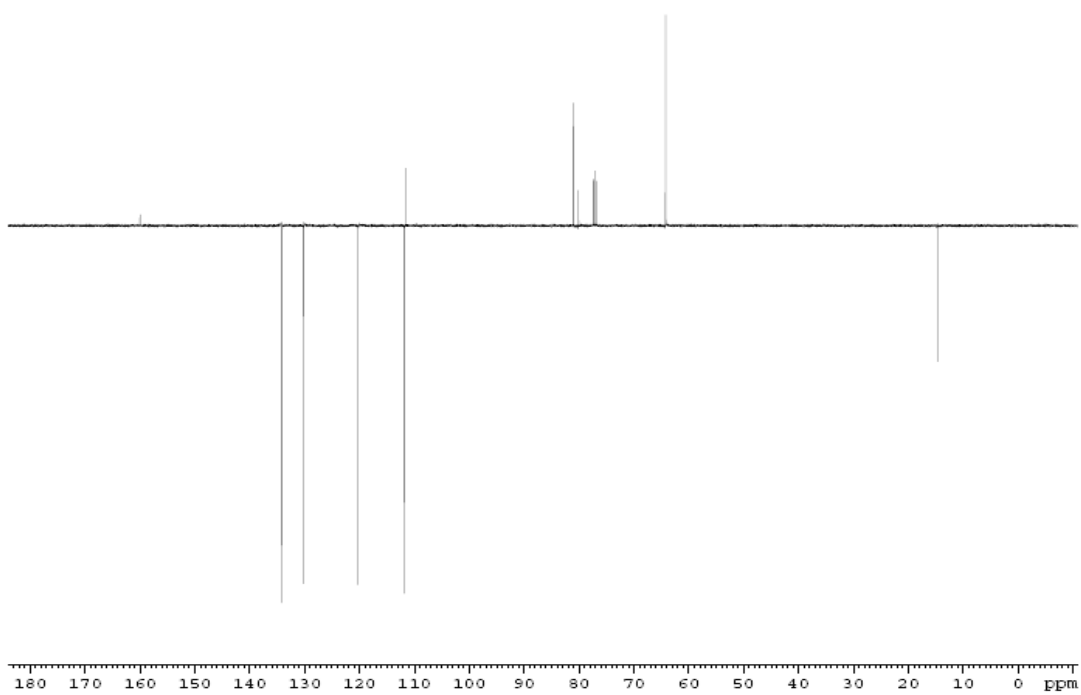
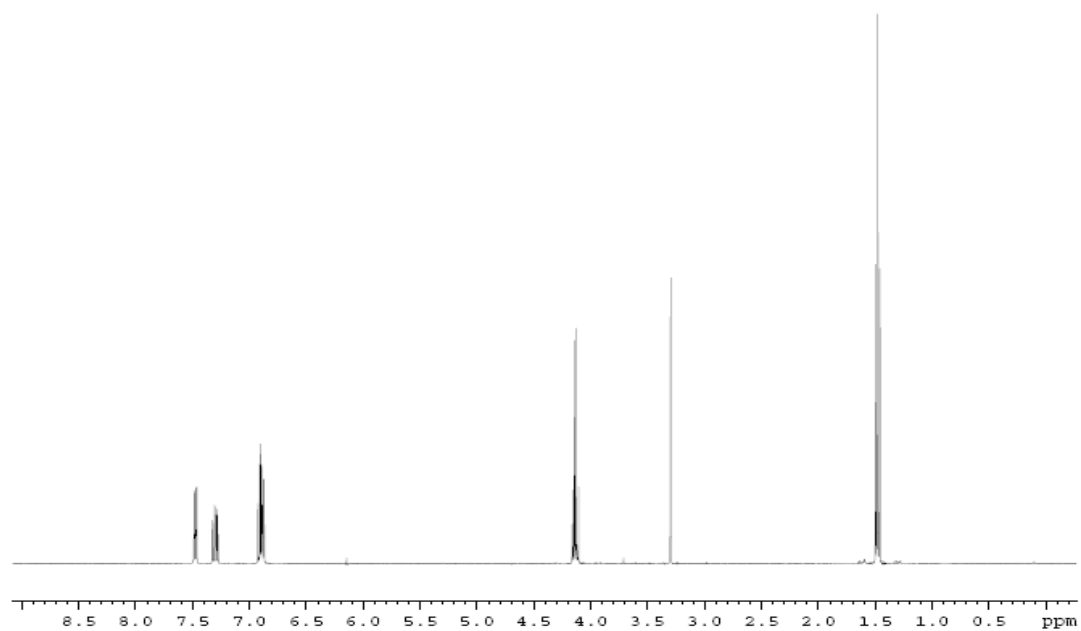


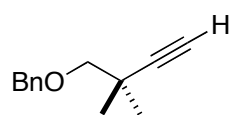
**2c**  $\text{CDCl}_3$ , 400 MHz



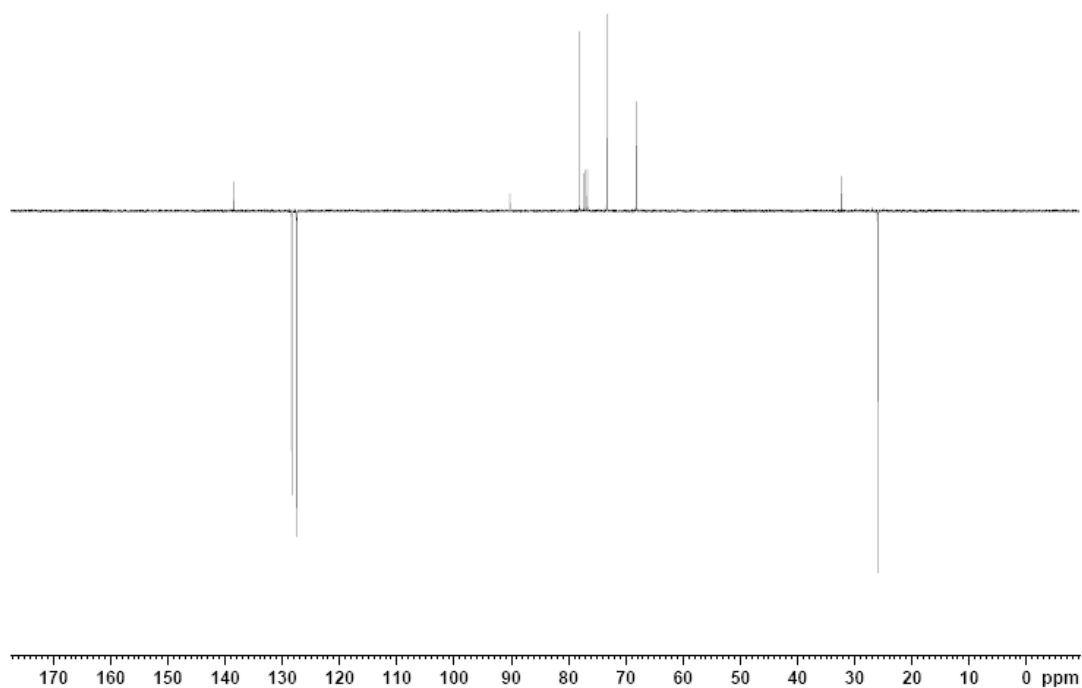
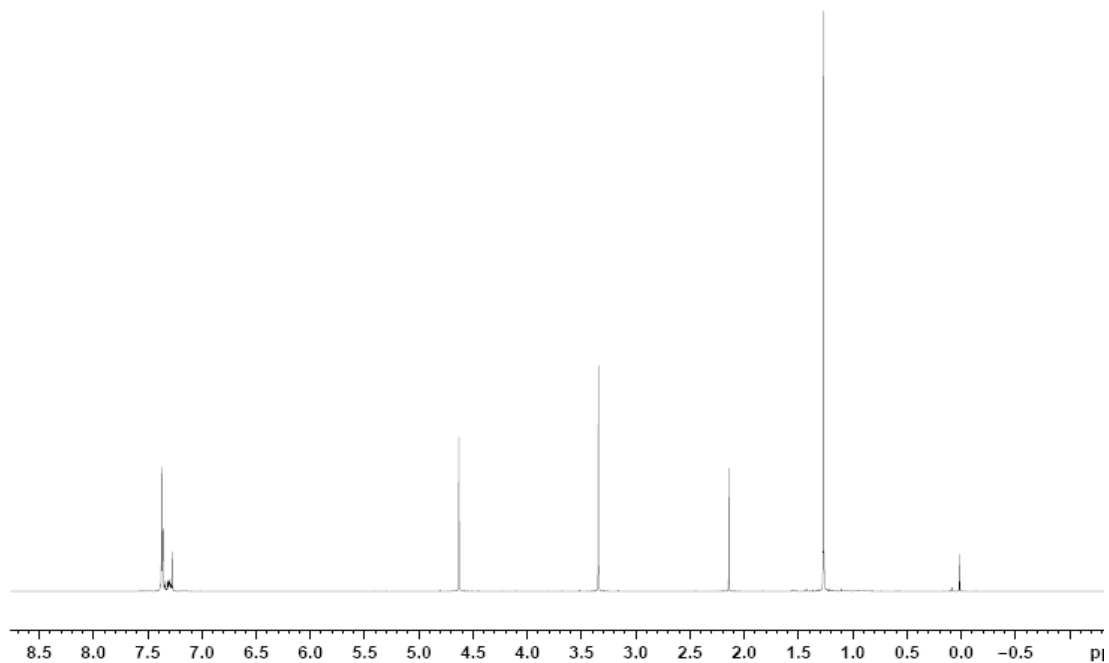


**2d** CDCl<sub>3</sub>, 400 MHz



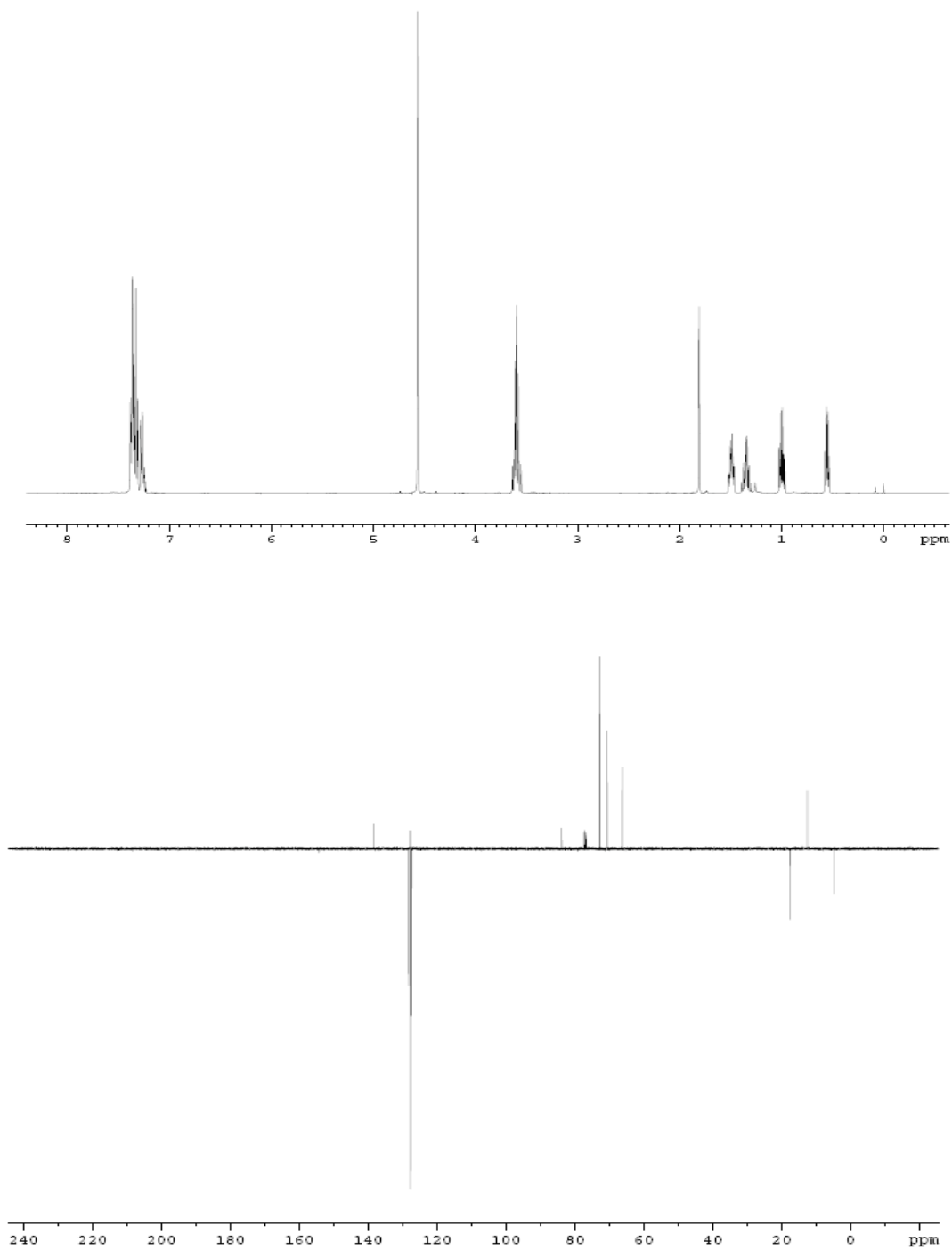


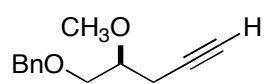
2e CDCl<sub>3</sub>, 400 MHz





**2f** CDCl<sub>3</sub>, 400 MHz





2g CDCl<sub>3</sub>, 400 MHz

